Investigating the efficiency of "in-house" produced hydrogels as internal curing agents in cement pastes

José Roberto Tenório Filho[1,2], Els Mannekens[3], Didier Snoeck[1], Nele De Belie[1]

[1]Magnel Laboratory for Concrete Research, Department of Structural Engineering, Faculty of Engineering and Architecture, Ghent University, Tech Lane Ghent Science Park, Campus Ardoyen, Technologiepark Zwijnaarde 60, B-9052 Gent, Belgium.

[2]SIM vzw, Technologiepark 48, Zwijnaarde B-9052 Ghent, Belgium.

[3]Chemstream bvba, Drie Eikenstraat 661, 2650 Edegem, Belgium.

ICSBM 2019
ID 049

Abstract

Appropriate curing is of utmost importance to guarantee that a concrete structure (or any cementitious material) achieves proper hydration and can provide the user with the best of its desired properties. For most of conventional concrete compositions external curing has proven to be effective, but the advent of the (ultra) high performance showed a different reality. Given its finer microstructure, the water from external curing methods cannot always penetrate the whole depth of the structure. External curing thus is not efficient in preventing problems such as cracking due to autogenous shrinkage, but a solution could be to include an internal curing system. Alternative inclusions such as lightweight aggregates and shrinkage-reducing admixture (SRA) have been studied and used as internal curing agents. Recently, researchers have been investigating the use of hydrogels or superabsorbent polymers for internal curing purposes and the results are promising. In this paper three different "in-house" produced polymers are studied as internal curing agents in cement pastes. The polymers differ in chemical composition leading to different properties. Initially they were tested for the water uptake in artificial cement pore solution by means of a filtration test and further tested in cement pastes with a range of w/c ratios from 0.30 to 0.40. Their efficiency as internal curing agents was assessed by means of autogenous shrinkage measurements with corrugated tubes for a period of seven days. All three polymers showed promising results in the mitigation of the autogenous shrinkage but two of them with the pitfall of requiring a higher amount of additional water. To summarize, the hydrogels are indeed interesting as internal curing agents but attention should be given to their chemical composition and physical aspects since for each application different properties are required.

Keywords: hydrogels, autogenous shrinkage, cement, superabsorbent polymers.

1. Introduction

Most of the deteriorating mechanisms acting on concrete structures are related to the ingress of aggressive agents inside structures. Even before reaching its hardened state, a cement-based material is subjected to crack formation especially due to the effects of shrinkage during the early age. The formed porosity of the material can become the perfect path for the ingress of those aggressive agents. After the formation the water intrusion causes a drop in pH of the concrete that can lead to steel corrosion; the ingress of

chlorides causes the de-passivation of the protective film, the intrusion of CO_2 can cause carbonation and both processes can accelerate the corrosion.

The shrinkage phenomena, especially when referring to autogenous and plastic shrinkage, are inherent to the hydration process of the cementitious material and (among other factors) are a function of the water-to-cement ratio and curing conditions (temperature and humidity). The autogenous shrinkage is related to the self-desiccation initiated in the pores of the material due to the hydration process [1].

Appropriate curing is of utmost importance to guarantee that a concrete structure (or any cementitious material) achieves proper hydration and can provide the user with the best of its desired properties. For most of conventional concrete compositions external curing has proven to be quite effective, but the advent of the (ultra) high performance showed a different reality. Given its finer microstructure, the water from external curing methods cannot always penetrate the whole depth of the structure. External curing thus is not efficient in preventing problems such as cracking due to autogenous shrinkage, but a solution could be to include an internal curing system. Alternative inclusions such as lightweight aggregates and shrinkage-reducing admixture (SRA) have been studied and used as internal curing agents. Recently, researchers have been investigating the use of hydrogels or superabsorbent polymers (SAPs) for internal curing purposes and the results are promising [2-4].

ICSBM 2019
ID 049

Superabsorbent polymers (or hydrogels) are a natural or synthetic water-insoluble 3D network of polymeric chains cross-linked by chemical or physical bonding. They possess the ability to take up a significant amount of fluids from the environment (in amounts up to 500 times their own weight). The swelling and posterior water release are of great interest in the study of smart self-healing materials but can also be explored to promote self-sealing [2-5]. In this paper, three different in-house produced SAPs are presented as alternative for promoting internal curing in cement pastes.

All SAPs are produced with different co-monomers (Figure 1), each of them being designed to have different swelling capacities. The required properties of the SAPs were based on the properties found in literature for commercially available SAPs aiming at a proper internal curing of cementitious materials.

The internal curing efficiency of the SAPs was evaluated by means of an autogenous shrinkage test. A filtration test and slump flow test were also performed to assess the water uptake by the SAPs and their influence in the workability of the mixtures.

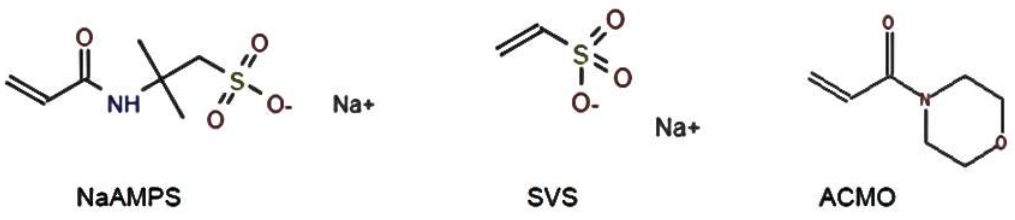

Figure 1: Co-monomers that were used in the SAPs from ChemStream.

2. Methodology

2.1 Materials

All tests were performed on cement pastes produced with cement type CEM III-B 42.5N – LH/SR; a polycarboxylate superplasticizer (at a constant dosage of 0.3 m% in relation to the cement mass; Glenium 51, 35% conc.); an effective water to cement ratio of 0.3; three different hydrogels (all in-house produced) with a dosage in the range of 0.023 m% to 0.4 m%. The composition of the studied mixtures can be found

in Table 1.

Table 1: Composition of the mixtures studied.

Mixture	Cement [kg/m³]	Mixing water [kg/m³]	Superplasticizer [kg/m³]	SAP [kg/m³] (m%)	Additional water [kg/m³]	w/c	
						Effective	Total
REF1	1620	486	4.86	0	0	0.3	0.3
REF2	1490	447	4.47	0	0	0.354	0.354
SAP1.1	1490	447	4.47	0.34 (0.023%)	80.46	0.3	0.354
SAP1.2	1198	359.4	3.59	1.31 (0.11%)	259.96	0.3	0.517
SAP2.1	1490	447	4.47	2.01 (0.135%)	80.46	0.3	0.354
SAP2.2	1393	417.9	4.17	2.78 (0.2%)	139.3	0.3	0.4
SAP3	1490	447	4.47	5.96 (0.4%)	80.46	0.3	0.354

All SAPs were produced by ChemStream and have been tested specifically for use in cementitious materials.

SAP type 1 is a SAP composed of 2 co-monomers NaAMPS (2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt) and SVS (sodium vinyl sulfonate) that are lightly cross-linked. Both co-monomers contain the sodium salt form of a sulphonic acid group, which leads to a very densely charged hydrogel with great osmotic power for absorbing water. This type of SAP-composition is based on ChemStream's prior art EP2835385.

SAP type 2 is a SAP that is similar to SAP type 1, since it mainly consists of co-monomer NaAMPS, but it is 'diluted' with a non-charged or neutral monomer ACMO (acryloyl morpholino acrylate) (20% mol).

SAP type 3 is also very similar to SAP type 1, because it is solely composed of monomer NaAMPS but with a lower absorption capacity.

More information on the properties of the SAPs can be found in Table 2.

Table 2: Properties of the SAPs.

SAP	Mean particle size D_{50} [µm]	Absorption capacity* [g/g]	Soluble materials [%]
SAP1	100	275	36
SAP2	100	261	9
SAP3	100	54	8

*For absorption in demineralized water after 24 hours

2.2 Methods

The absorption capacity of the SAPs was evaluated by means of a filtration test using cement filtrate (1 kg of cement CEM III-B 42.5N – LH/SR and 5 l of demineralized water) at 10 min and 24h after the first contact of the dry hydrogels with water.

Afterwards the absorption capacity in real cement pore fluid was assessed by means of slump flow test with the cement pastes mentioned in Table 1. The principle of this test is to add a certain amount of SAPs to a cement paste with w/c of 0.354 (theoretical value for a complete hydration of the system according to [6, 7]) until the slump flow measured equals the value of the reference cement paste REF1. By doing so, it is assumed that the difference in water content of both reference mixtures (w/c of 0.054) is totally absorbed

by the SAPs. The average slump of the reference mixture REF1 was 300 ± 15 mm. The measurements were performed after 10 min counted from the moment the water was added to the mixture.

The internal curing effect of the SAPs was evaluated by means of a shrinkage test, performed with corrugated tubes, in compliance with ASTM C1698-09. The measurements of deformation were performed automatically with linear variable differential transducers (LVDT) with a range of 5 mm (Figure 2). From the total deformation curve, the autogenous shrinkage strain was calculated zeroing the deformations at the knee-points of the original curves [8] (Figure 3).

Figure 2: Set up for the autogenous shrinkage measurement.

In some cases, the amount of SAP determined to absorb the additional amount of water corresponding to the additional 0.054 in the w/c ratio was not enough to completely mitigate the autogenous shrinkage of the mixture. For those cases, the amount of SAP was increased and the additional water inserted in the system was corrected to achieve a fully mitigation of the autogenous shrinkage. This justifies the existence of mixtures SAP1.2 and SAP2.2 (shown in Table 1) for which results will be presented in the following section.

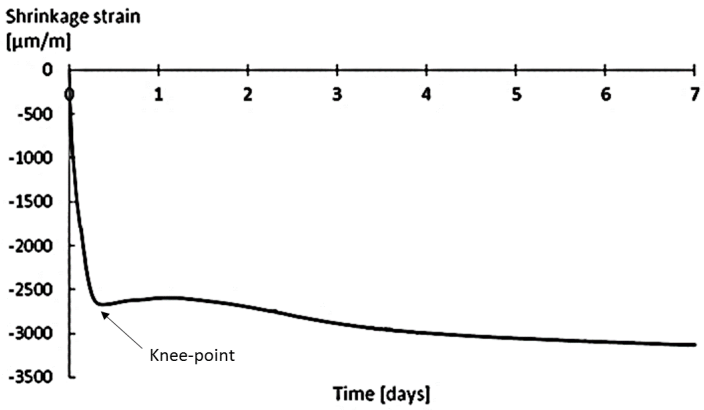

Figure 3: Illustration of the knee-point in the shrinkage strain curve over time for a cement paste.

3. Results and discussion

The absorption capacity of the SAPs in the different media shows different trends in behavior for the studied hydrogels (Figure 4).

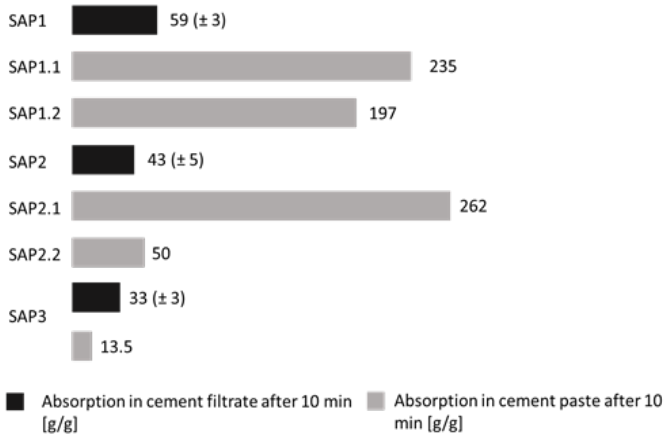

Figure 4: SAP1 and SAP2 present a higher absorption capacity in cement paste in comparison with cement filtrate. SAP3 shows the opposite.

SAP1 and SAP2 both present a higher absorption capacity in the cement paste in comparison to the cement filtrate solution. The opposite was noticed with SAP3, which is in accordance to the behavior of commercially available hydrogels reported in other studies [9]. By increasing the amount of SAPs in the system (mixtures SAP 1.2, and SAP 2.2) the increase in the required additional water did not show a linear behavior. This is also mentioned by [10] and can be explained by the change in the concentration of ions in the system that occurs when more water is added and its influence on the sorption/desorption kinetics of SAPs.

In terms of chemical composition, SAP1 is more densely charged in comparison to SAP2 and SAP3 which theoretically would lead to a higher absorption capacity. The fact the this absorption is higher in the cement paste in comparison to the cement filtrate shows evidence that more variables are influencing the kinetics of the SAPs once they are in contact with the paste (the presence of superplasticizer, for example).

The results for autogenous shrinkage of the mixtures are show in Figure 5.

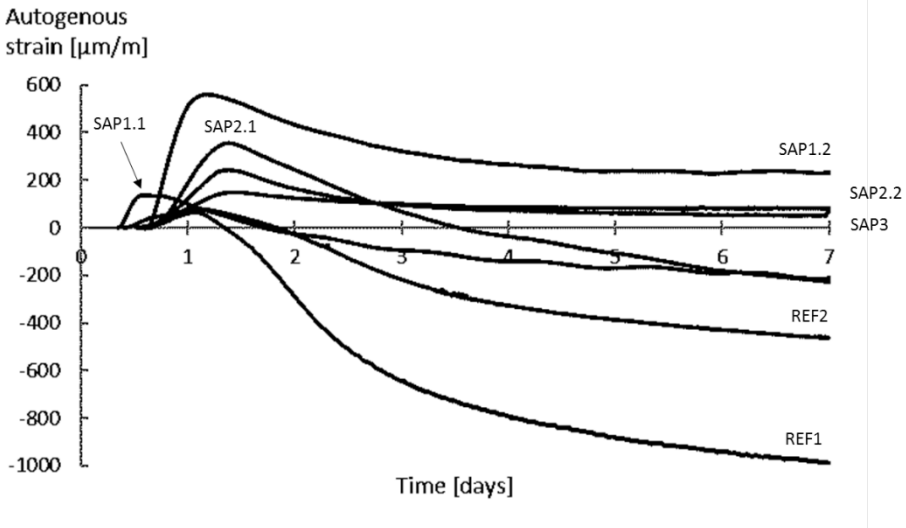

Figure 5: All SAPs promote a reduction in the autogenous strain of the cement paste in comparison to the references without SAPs. SAP3 shows the most promising result in terms of additional water and effective internal curing.

All SAPs promote a reduction in the autogenous strain in comparison to the both references. Considering only the mixtures SAP1.1, SAP2.1 and SAP3 in comparison with the REF2 (all of them with the same total

w/c ratio) only SAP3 is able to completely mitigate the autogenous shrinkage. Still, both mixtures SAP1.1 and SAP2.1 show a shrinkage strain lower than the reference.

In both mixtures SAP1.2 and SAP2.2 there is complete mitigation of the autogenous shrinkage during the complete period of testing (seven days). However, the total w/c ratio of both mixtures is higher in comparison to the references (0.517 and 0.4). In that case, in order to verify the real efficiency of the SAPs in those mixtures, new references should be mixed with the same w/c ratios (0.517 and 0.4) to assess till what extent the mitigation of shrinkage is due to the controlled released of water promoted by the SAPs or due to the higher amount of free water in the system. Also for clarification of that matter, the water release of the SAPs in the mixtures should be investigated, especially for SAP1 and SAP2. This should reveal why SAP3 showed a completely mitigation of the autogenous shrinkage with the same w/c ratio as REF2 while the other SAPs needed to be added in a dosage higher than initially defined.

4. Conclusions

Despite the differences in chemical composition and properties, all SAPs showed promising results. In the range of 0.2-0.4 m% a complete mitigation of autogenous shrinkage was obtained with a very small increase in the total w/c of the mixtures and an amount of 0.1% led to a reduction of around 80% in the shrinkage strain.

SAP1 and SAP2 showed a different behavior depending on the amount of SAP and water in the system, in comparison with SAP3. Further study is needed to investigate the kinetics of water release by the SAPs in the different situations presented in this paper.

The addition of SAPs and water in the system might also have effects (not only positive) on other aspects of the cementitious materials such as mechanical strength, setting time, microstructure and so on. All these influences should be taken into account when deciding to use a specific type of SAP and a balance should be made between its positive and negative influences in order to choose the SAP that best suits a certain application.

ICSBM 2019
ID 049

5. Acknowledgment

The work has been financed by SIM program SHE (Engineered Self-Healing Materials) within the ICON project iSAP (Innovative SuperAbsorbent Polymers for crack mitigation and increased service life of concrete structures).

6. References

[1] Sahinagic-Isovic, M., Markovski, G., Cecez, Marko. Shrinkage strain of concrete – causes and types. Journal of the Croatian Association of Civil Engineers, GRADEVINAR 64 9, 727-734. 2012.

[2] Snoeck, D. Self-Healing and Microstructure of Cementitious Materials with Microfibres and Superabsorbent Polymers. Doctorate thesis – Faculty of Architecture and Engineering/Ghent University. Belgium, 2015.

[3] Mechtcherine, V., Dudziak, L., & Hempel, S. Mitigating early age shrinkage of Ultra-High-Performance Concrete by using Super Absorbent Polymers (SAP). Paper presented at the Creep, Shrinkage and Durability Mechanics of Concrete and Concrete Structures, Ise-Shima, Taylor & Francis, 847-853. 2009.

[4] Jensen, O.M. Use of superabsorbent polymers in construction materials. Paper presented at the International Conference on Microstructure Related Durability of Cementitious Composites, Nanjing, RILEM Publications S.A.R.L., 757-764. 2008.

[5] Mignon, A., Snoeck, D., Dubruel, P., Van Vlierberghe, S., De Belie, N. Crack mitigation in concrete : superabsorbent polymers as key to success? Materials, 10(3), 237. 2017.

[6] Powers, T.C., & Brownyard, T.L. Studies of the physical properties of hardened Portland cement paste (Vol. 22). Cornell: Portland Cement Association, Research Laboratories, pp. 892. 1948.

[7] Jensen, O.M., & Hansen, P.F. Water-entrained cement-based materials I. Principles and theoretical background. Cement and Concrete Research, 31(4), 647-654. 2001.

[8] Lyu, Y. Autogenous Shrinkage of Cement-Based Materials: From the Fundamental Role of Self-Desiccation to Mitigation Strategies Based on Alternative Materials. Doctorate thesis – Faculty of Architecture and Engineering/Ghent University. Belgium, 2017.

[9] Tenório Filho, José Roberto; Snoeck, D. ; Belie, N. . The effect of superabsorbent polymers on the cracking behavior due to autogenous shrinkage of cement-based materials. In: 60 Congresso Brasileiro do Concreto, 2018, Foz do Iguaçu. Anais do 60 Congresso Brasileiro do Concreto, 2018.

[10] Ma, X., Yuan, Q., Liu, J., Shi, C. Effect of water absorption of SAP on the rheological properties of cement-based materials with ultra-low w/b ratio. Construction and Building Materials, 195, 66-74. 2019.

ICSBM 2019
ID 049